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(71) Applicant: THE BOARD OF TRUSTEES OF THE LELAND STANFORD JUNIOR UNIVERSITY [US/US]; 900 Welch Road, Suite 350, Palo Alto, CA 94304-1850 (US).

(72) Inventors: DAI, Hongjie; 365 Pescadero Tr., Sunnyvale, CA 94507 (US). FAN, Shoushan; Building SW5-1-402, Tsinghua University, Beijing (CN). CHAPLINE, Michael; 2504 Round Hill Drive, Alamo, CA 94507 (US). FRANKLIN, Nathan; 350 Sharon Park Drive, #H-205, Menlo Park, CA 94025 (US). TOMBLER, Thomas, Jr.; 121 Campus Drive, Apartment 1409A, Stanford, CA 94305 (US).

(74) Agent: ALBOSZTA, Marek; 426 Lowell Avenue, Palo Alto, CA 94301 (US).

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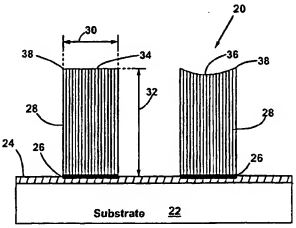
(54) Title: SELF-ORIENTED BUNDLES OF CARBON NANOTUBES AND METHOD OF MAKING SAME



(57) Abstract

A field emission device (20) having bundles (28) of aligned parallel carbon nanotubes on a substrate (22). The carbon nanotubes (28) are oriented perpendicular to the substrate (22). The carbon nanotube bundles (28) may be up to 300 microns tall, for example. The bundles (28) of carbon nanotubes extend only from regions of the substrate (22) patterned with a catalyst material (26). Preferably, the catalyst material (26) is iron oxide. The substrate (22) is preferably porous silicon, as this produces the highest quality, most well-aligned nanotubes. Smooth, nonporous silicon or quartz can also be used as the substrate. The method of the invention starts with forming a porous layer on a silicon substrate by electrochemical etching. Then, a thin layer of iron is deposited on the porous layer in patterned regions. The iron is then oxidized into iron oxide, and then the substrate is exposed to ethylene gas at elevated temperature. The iron oxide catalyzes the formation of bundles of temperature. The iron oxide catalyses the formation of bundles of aligned parallel carbon nanotubes which grow perpendicular to the substrate surface. The height of the nanotube bundles above the substrate is determined by the duration of the catalysis step. The nanotube bundles only grow from the patterned regions.

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PCT Patent Application entitled

Self-Oriented Bundles of Carbon Nanotubes and Method of Making Same

FIELD OF THE INVENTION

This invention relates generally to carbon nanotubes. The present invention also relates to methods for making bundles of aligned carbon nanotubes. The present invention is also related to carbon nanotube field emission devices such as used in flat panel displays.

BACKGROUND

Field emission devices have potential applications in flat panel displays. Field emitters used in flat panel displays must be stable, long lasting and should have a relatively uniform emission over the surface of the display.

Carbon nanotubes are very small tube-shaped molecules having the structure of a graphite molecule rolled into a tube. Carbon nanotubes are electrically conductive along their length, chemically stable, and can have very small diameters (much less than 100 nanometers) and large aspect ratios (length/diameter). Due to these properties and other properties, it has been suggested that carbon nanotubes can be used as field emission devices.

However, it has been unclear how to realize a field emission device exploiting carbon nanotubes. They are difficult to work with in bulk, and, on a microscopic level, often form an impossibly tangled mess resembling a hairball. To produce a useful field emission device for flat panel displays, the carbon

nanotubes should be patterned into individual field emitters. A problem with present methods of making carbon nanotube field emitters it that it is not clear how to pattern the carbon nanotube to provide arrays of emitters.

US Patent no. 5,773,921 to Keesman et al. discloses a field emission device which employs sharp-edged graphite wafers. Carbon nanotubes are disposed on the sharp edge of the graphite wafers and help to increase field emission. The carbon nanotubes are disposed on the graphite wafers by sputtering a nearby graphite target. The carbon nanotubes are not aligned in any way.

US Patent no. 4,272,699 to Faubel et al. discloses an ion source which uses carbon fiber field emitters. The carbon fibers are bundled together and an electric field is applied to the bundle. The carbon fibers are held by a macroscopic mechanical device that holds the fibers parallel. Such a mechanical device cannot be used with carbon nanotubes, which are orders of magnitude smaller than the carbon fibers used by Faubel et al.

US Patent no. 5,773,834 to Yamamoto et al. describes a method of making carbon nanotubes on the surface of a carbon-containing substrate by ion bombardment. The carbon nanotubes produced can be used as field emitters. The carbon nanotubes produced according to Yamamoto are not aligned, and in particular, are not aligned perpendicular to the substrate. Also, Yamamoto does not disclose how to pattern the substrate to provide individual field emitters.

Yet another problem with present methods for making carbon nanotube field emitters is that scale-up to large wafers is difficult or not possible.

There exists a need in the art for a method of producing aligned carbon nanotubes. In particular, such aligned carbon nanotubes can be used as superior field emission devices.

OBJECTS AND ADVANTAGES

Accordingly, it is a primary object of the present invention to provide:

1) a method of making aligned bundles of carbon nanotubes; and

2) a field emission device using aligned bundles of carbon nanotubes as field emitters;

3) a field emission device that can have arrays of emitters;

4) a method of making field emitters that can be scaled to large substrates.

These and other objects and advantages will be apparent upon reading the following description and accompanying drawings.

SUMMARY

These objects and advantages are attained by a field emission device having a refractory substrate composed of silicon or quartz, a catalyst material on top of the substrate, and a bundle of aligned parallel carbon nanotubes extending from the catalyst material in a direction perpendicular to the substrate.

Preferably, the substrate has a top layer of porous silicon, with the catalyst material disposed on the porous layer. Particularly, the porous layer can be composed of an upper nanoporous layer with small pores on top of a macroscopic porous layer with larger pores. The catalyst material is preferably iron oxide.

The substrate my also have a smooth, nonporous surface, or a rough surface.

The carbon nanotube bundles may be within 10-22 nanometers in diameter and may be up to 300 microns tall. Also, the carbon nanotubes my be multi-walled.

Preferably, the catalyst material is confined to a patterned region. This results in the bundle extending from the patterned

region. The bundle has the same footprint size and shape as the patterned region of the catalyst material.

The carbon nanotube bundles may have a flat top, or a bowl-shaped top.

The present invention also includes a method of making bundles of aligned carbon nanotubes on a substrate of silicon or quartz. The method includes the steps of depositing a catalyst material on a top surface of the substrate, and then exposing the substrate to a carbon containing gas.

Preferably, the substrate is a silicon substrate with a porous top surface. The top surface may be made porous by electrochemical etching.

The catalyst material is preferably iron oxide. The iron oxide may be deposited by depositing a thin film of iron, and then oxidizing the iron film. The iron film may be oxidized by exposing it to oxygen at elevated temperature. Preferably, the original iron film is bout 5 nanometers thick.

The carbon containing gas may be ethylene.

DESCRIPTION OF THE FIGURES

Fig. **1** shows a field emission device according to the present invention.

Fig. **2** shows a graph of field emission characteristics of a field emission device according to the present invention.

Fig. **3** illustrates a method according to the present invention for making bundles of aligned carbon nanotubes on a porous silicon substrate.

Fig. **4** illustrates a methods according to the present invention for making bundles of aligned carbon nanotubes on a smooth, nonporous silicon substrate.

Fig. **5** shows a field emission device with many nanotube bundles. Each bundle can provide field emission to illuminate a single pixel in a flat panel display.

DETAILED DESCRIPTION

Fig. 1 shows a field emission device **20** according to a preferred embodiment of the present invention. The device has a substrate **22** with a porous top layer **24**. The substrate **22** and top layer **24** are made of silicon, although other substrate materials can also be used. Disposed on the porous top layer **24** are patterns of catalyst material **26**. Preferably, the catalyst material **26** is a thin film of iron oxide. Extending from the catalyst material patterns **26** are carbon nanotube bundles **28**, which are perpendicular to the substrate **22**. The carbon nanotubes comprising the bundles are parallel and perpendicular to the substrate **22**. The carbon nanotubes comprising the bundles are typically about 10-22 nanometers in diameter.

The bundles **28** may be about 10-250 microns wide **30**, and up to or exceeding 300 microns in height **32**. The nanotube bundles have the same width **30** as the catalyst material patterns **26**. More generally, the bundles **28** have the same 'footprint' size and shape as the catalyst meterial patterns **26**. The nanotube bundles **28** can have a flat top **34**, or can have a bowl-shaped top **36**, depending on the process parameters used to make the nanotube bundles. There are no individual stray nanotubes extending away from the blocks.

The nanotube bundles **28** have sharp edges **38** and corners which serve as field emission regions. Since the substrate can be conductive (e.g. doped silicon) and the nanotubes are conductive along their length (parallel with height **32**), electrical connections to the bundles **28** are made simply by connecting to the substrate **22**.

Fig. 2 shows field emission characteristics for four nanotube bundles on a n^+ type silicon substrate. The bundles each have a footprint of 250 microns X 250 microns and are 160 microns tall. The anode is an aluminum coated silicon wafer 200 microns above the substrate. The data is taken in a vacuum chamber at 3×10^{-7} Torr base pressure. Note that the electric field is computed by using the applied voltage divided by the distance from the tops of the bundles to the anode (40 microns). The current density

reaches 10mA/cm^2 at an electric field strength of 5 volts/micron. After continuous emission for a week at 2mA/cm^2 the bundles show no indication of damage under a scanning electron microscope.

The present invention includes methods of making the carbon nanotube bundles attached to substrates. **Fig. 3** illustrates a preferred method for making the nanotube bundles. First, in step **A**, a highly P-doped n$^+$ type silicon substrate **22** (100 top surface, resistivity 0.008-0.018 Ohm-cm) is electrochemically etched in 1:1 HF (49% in water) ethanol with an anodization current density of 10mA/cm^2 (typical etching time is 5 minutes). This forms a thin nanoporous layer **42** (pore size~3 nanometers) on top of a macroporous layer **44** (pore size~100 nanometers). Layers **42**, **44** are generally referred to as a porous layer **24** in **Fig. 1**. Next, in step **B**, the porous layer **42** is patterned with a 5 nanometer thick iron film **46** by e-beam evaporation through a shadowmask **48**. After deposition of iron, the substrate is annealed in air at 300°C overnight. This annealing step oxidizes the surface of the silicon as well as the iron, converting the iron patterns **46** into catalytically active iron oxide patterns **26**. The resulting silicon dioxide layer formed on the porous silicon prevents the porous structure of layers **42**, **44** from collapsing during the following high temperature chemical vapor deposition (CVD) step. Next, in step **C**, the substrate **22** is placed in a 2-inch tube reactor **49** housed in a tube furnace. The furnace is heated to 700°C in flowing argon. Then, at 700°C, the argon supply is turned off, and ethylene **50** is flown through the tube reactor at a rate of 1000 sccm/min for 15-60 minutes. The boat for the substrates is sealed at one end, and the sealed end is placed downstream in the furnace. While ethylene **50** is flowing, the iron oxide patterns **26** catalyze the growth of carbon nanotube bundles **28** which grow perpendicular to the substrate **22**. The width of the bundles **28** is the same as the width of the iron oxide patterns **26**.

The above method for makfing nanotube bundles produces mainly flat-top bundles, although sometimes bowl-shaped bundles are also produced. Bowl-shaped bundles are produced when nanotubes in the middle of a bundle grow slower than the nanotubes at the outer edges of a bundle.

The height of the bundles **28** is determined by the duration that the substrates are exposed to ethylene at high temperature. In a particular experiment conducted by applicants, reaction times of 5, 15, 30, and 60 minutes produced bundles 31, 98, 163, and 240 microns tall, respectively. The growth rate is observed to be linear initially and then falls off at longer reaction times. As the aspect ratio (height:width) of the bundles approaches 5:1, some bundles may become tilted, but refuse to fall down.

The bundles can have footprint sizes as small as 2 microns on a side and be 15 microns tall, and still remain standing on the substrate.

Since the carbon nanotubes grow only from those regions that have deposited iron oxide, patterning the iron oxide results in carbon nanotubes growing only from those regions with iron oxide. This provides accurate control of the size, shape, and distribution of the bundles on the substrate surface. As a particular advantage, patterning of the catalyst provides the ability to fabricate arrays of individual field emitters. Each bundle can provide field emission for a single pixel in a flat panel display. Each bundle can be individually controlled by connecting patterned metallization lines to the bundles. Further, the arrays can be formed on large substrates. The size of the substrate is only limited by the size of the tube furnace. The substrate can be several inches across, for example. Many field emitter arrys have been fabricated on 3cm X 3cm silicon substrates.

The method of the present invention produces carbon nanotube bundles having a high density. The nanotubes are held together by Van der Waals interactions. The nanotubes grown according to the present method are in the size range of about 16±6 nanometers and are aligned parallel in a direction perpendicular to the substrate **22**. The carbon nanotubes are aligned perpendicular to the substrate regardless of the orientation of the substrate in the furnace. The carbon nanotubes are generally multi-walled.

The porous layer acts as an excellent catalyst support. During the 300°C annealing step, iron oxide particles form with a narrow size distribution due to their strong interactions with the porous layer. The strong interactions also prevent the iron oxide particles from sintering at elevated temperatures.

It has been confirmed by the applicants that the nanotube bundles grow in 'base growth' mode. This has been established by physically removing nanotube bundles from the substrate and observing that the substrates remain capable of growing carbon nanotubes (i.e. the iron oxide catalyst patterns remain on the substrate).

The present method of growing aligned nanotubes is very different from prior art approaches of growing aligned nanotubes. In prior art approaches, carbon nanotube alignment is provided by confining the growth of nanotubes to channels in porous silica or the channels of alumina membranes. In the present method, the carbon nanotubes are self aligned, without being confined to a channel, pore, or hole. The carbon nanotubes of the present method spontaneously align themselves in free space.

It is important to note that the holes and pores in the porous layers **42**, **44** are not aligned or oriented in any way. For example, they are not necessarily aligned perpendicular to the substrate **22**. The holes and pores of the porous layer **24** generally have random orientations.

The present invention also includes a method of producing aligned carbon nanotubes on a nonporous smooth silicon substrate. The present method for growing aligned carbon nanotubes on nonporous silicon substrates is largely the same as the method for porous substrates. **Fig. 4** illustrates a first step in the present method for producing aligned carbon nanotube bundles on a smooth nonporous silicon substrate **40**. A thin film (e.g. 5 nanometers thick) of iron **46** is deposited through a shadowmask **48** using the same technique as in step **B** of **Fig. 3**. The nonporous substrate **40** has a native oxide layer which is left intact prior to the iron deposition. The 300°C annealing and 700°C CVD nanotube growth

steps for nonporous substrates **40** are the same as in the method described above for porous substrates. The CVD process forms carbon nanotube bundles which extend from iron oxide patterns perpendicularly to the nonporous substrate **40**.

The overall features of carbon nanotubes grown on nonporous silicon are similar to the features of nanotubes grown on porous silicon. However, in contrast to porous silicon substrates, nanotube bundles with aspect ratios greater than 5 tend to fall onto the substrate **40**. Nanotube bundles grown on smooth nonporous substrates are not as strongly bound to the substrate. Also, carbon nanotube bundles grown on nonporous silicon substrates tend to have higher defect densities, and tend to be less well aligned than bundles grown on porous silicon. Further, carbon nanotubes grow about 50% faster on porous silicon compared to nonporous silicon. For these reasons, the use of porous silicon substrates is highly preferred.

Fig. 5 shows a field emission device that can be used in a flat panel display. The device has many carbon nanotube bundles **28**. Each bundle **28** can provide field emission for a single pixel in a flat panel display.

It is also noted that the iron catalyst does not necessarily need to be deposited using physical vapor deposition techniques, although this is preferred. For example, catalyst materials can be deposited as iron salts dissolved in a carrier solvent. The solvent is then deposited on the substrate and allowed to dry, leaving the iron salt. The iron salt may then need to be 'activated' by exposing it to high temperature so that it decomposes into active catalyst material.

It is also noted that the substrate does not necessarily need to be silicon, although silicon, and particularly, porous silicon, is preferred. The substrate can also be quartz. In the present application, silicon, porous silicon, and quartz are understood to be refractory materials.

The present method for making bundles of aligned carbon nanotubes may also work on substrates such as ceramics, alumina, sapphire, and silica, for example. The substrate must be able to tolerate the high temperatures (about 700°C) used in the CVD process without meting or disintegrating. For best results, the substrate should have a rough and complex surface topology.

It is also noted that the substrate can have a rough texture which is neither smooth nor 'porous'. Generally, however, extremely complex substrate surface topologies are preferred because they produce fast growing nanotubes with few defects that are strongly bound to the substrate.

It will be clear to one skilled in the art that the above embodiment may be altered in many ways without departing from the scope of the invention. Accordingly, the scope of the invention should be determined by the following claims and their legal equivalents.

CLAIMS

What is claimed is:

1. A field emission device comprising:

a) a substrate composed of refractory material;

b) a catalyst material deposited on a top surface of the substrate;

c) a bundle of parallel carbon nanotubes extending from the catalyst material in a direction perpendicular to the substrate.

2. The field emission device of claim 1 wherein the substrate is a silicon substrate.

3. The field emission device of claim 2 wherein the silicon substrate has a porous top layer and the catalyst material is disposed on the porous top layer.

4. The field emission device of claim 3 wherein the porous top layer comprises a first porous layer on top of a second porous layer, and wherein the pores of the first layer are smaller than the pores of the second layer.

5. The field emission device of claim 1 wherein the catalyst material comprises iron oxide.

6. The field emission device of claim 1 wherein the silicon substrate has a smooth top surface.

7. The field emission device of claim 1 wherein the silicon substrate has a rough top surface.

8. The field emission device of claim 1 wherein the carbon nanotubes have diameters in the range of 10-22 nanometers.

9. The field emission device of claim 1 wherein the carbon nanotubes are multi-walled.

10. The field emission device of claim 1 wherein the carbon nanotube bundles are less than 300 microns tall.

11. The field emission device of claim 1 wherein the catalyst material is confined to a patterned region.

12. The field emission device of claim 11 wherein the carbon nanotube bundle has the same footprint size and shape as the patterned region.

13. The field emission device of claim 1 wherein the carbon nanotube bundle has a flat top.

14. The field emission device of claim 1 wherein the carbon nanotube bundle has a bowl-shaped top.

15. A method of making bundles of aligned carbon nanotubes on a top surface of a refractory substrate, the method comprising the steps of:

a) depositing a catalyst material on the top surface of the refractory substrate;

b) exposing the catalyst material to a carbon containing gas at elevated temperature.

16. The field emission device of claim 15 wherein the substrate is a silicon substrate.

17. The method of claim 16 further comprising the step of forming a porous top layer on the silicon substrate before step (a).

18. The method of claim 17 wherein the porous top layer is produced by electrochemical etching.

19. The method of claim 15 wherein the catalyst material comprises iron oxide particles.

20. The method of claim 15 wherein step (a) comprises the steps of depositing an iron film and then oxidizing the iron film.

21. The method of claim 20 wherein oxidation of the iron film is performed by exposing the iron film to oxygen at elevated temperature.

22. The method of claim 20 wherein deposition of the iron film is performed by physical vapor deposition.

23. The method of claim 20 wherein the iron film is 5 nanometers thick.

24. The method of claim 15 wherein the carbon containing gas is ethylene.

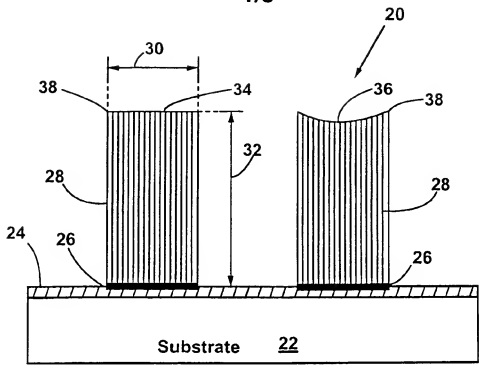
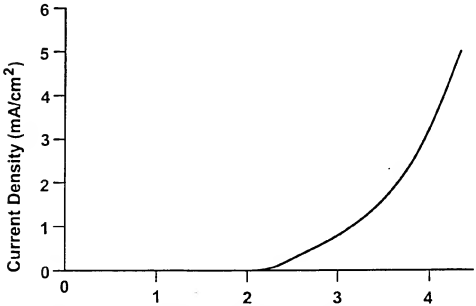

20
30
38
34
36
38
32
28
28
24
26
26
Substrate 22

Fig. 1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6
0
1
2
3
4
Electric Field (Volts/micron)

Fig. 2

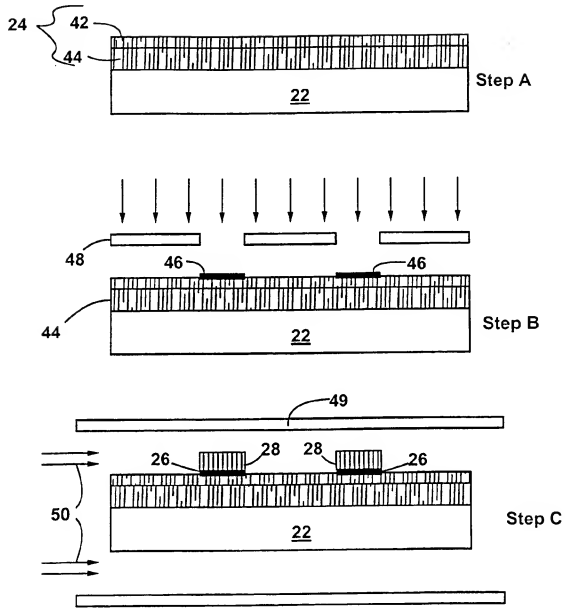

Fig. 3

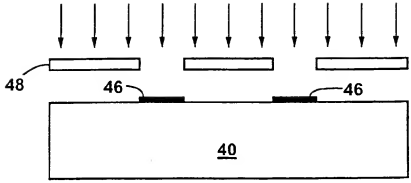

Fig. 4

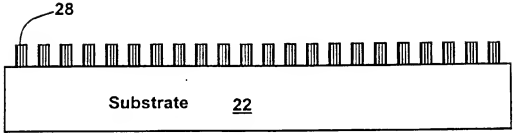

Fig. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/26232

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :H01J 01/30; C23C 16/00

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 313/309, 310, 336, 351, 346R, 494; 427/ 58, 255.6, 508, 521, 577, 578, 579, 249, 250, 255, 255.1; 204/192.1, 192.38

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X, P	US 5,872,422 A (XU et al.) 16 February 1999 (16.02.99), col. 5, line 8-col. 21, line 67.	1-24
X, P	US 5,973,444 A (XU et al.) 26 October 1999 (26.10.99), col. 5, line 9-col. 22, line 6.	1-24
A	US 4,272,699 A (FAUBEL et al.) 09 June 1981 (09.06.81), See entire document.	1-24
A	US 5,697,827 A (RABINOWITZ) 16 December 1997 (16.12.97), See entire document.	1-24
A	US 5,726,524 A (DEBE) 10 March 1998 (10.03.98), See entire document.	1-24
A	US 5,773,921 A (KEESMANN et al.) 30 June 1998 (30.06.98), See entrie document.	1-24

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search 15 JANUARY 2000	Date of mailing of the international search report 17 FEB 2000
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer MACK HAYNES Telephone No. (703) 308-0956

Form PCT/ISA/210 (second sheet)(July 1992)*

International application No.
PCT/US99/26232

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

313/309, 310, 336, 351, 346R, 494; 427/ 58, 255.6, 508, 521, 577, 578, 579, 249, 250, 255, 255.1; 204/192.1, 192.38